

Description of DE2438153

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Verfahren zur selektiven Entfernung von Acetylen aus dem bei der 1,2-Dichloräthan-Spaltung zu Vinylchlorid anfallenden

Crude hydrogen chloride contained gas mixture

The invention relates to a method to the selective distance he nung of acetylene from during the vinyl chloride production by cleavage of 1,2-Dichloräthan the resultant and after the separation of the vinyl chloride remaining, predominant

Hydrogen chloride contained gas mixture.

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Vinyl chloride becomes either pure thermal, i.e. without presence of catalysts, or in presence of catalysts with higher temperature from 1,2-Dichloräthan bottom cleavage of hydrogen chloride prepared. After separation of the major amount of the vinyl chloride a hydrogen chloride gas results, which has the subsequent approximate composition: > 99,5 Vol% hydrogen chloride 1.500 - 2.500 Vppm acetylene

50 - 300 "Vinylchlorid

100 - 200 "ethylen

50 - 100 flat steel bars Met; san before the use of this hydrogen chloride for chlorination reactions it is required to remove in an intermediate stage the disturbing acetylene contents of the gas mixture as to a large extent as possible.

This is done for example via catalytic hydrogenation, whereby the applied method is to fulfill the subsequent requirements: It is to remove as selective an acetylene as possible. Even with high cross section loads in the catalyst bed the acetylene contents of the hydrogen chloride is to become on lie close-conditional values of bottom 30 Vppm brought. An attachment of hydrogen chloride at acetylene is to become by favorable adjustment of the methods parameter avoided, since the resultant vinyl chloride poisons light polymerized and the catalyst necessary to the method. Vinyl chloride responsive with chlorines just like ethylen. It forms thereby however undesirable Nebenprodukte.Um variations in the total method to avoid, is Hydrierb dingl ngen, like e.g. Pressure, temperature, nLirchsat, if possible constant maintained to become to be able.

It is known, a method to the selective removal from acetylene with the Vinylchloridherstellung by cleavage of 1,2-Dichloräthan resultant and after the separation of the vinyl chloride remaining to be used predominant hydrogen chloride contained gas mixture with which one the gas mixture at a fixed bed catalyst, which exhibits the subsequent characteristic characteristic data, with a wasserstoffhaltigen gas trembling and ELT:

Carrier material: Active alumina

Active metal: Palladium BST surface: 50 - 300 m<sup>2</sup>/g

Pd-content: 0,1 - 0,2 thread.

Particle size: 1 - 3 mm (Strangpresslinge) the method in accordance with the state of the art supplies however, e.g.

by acetylene dismantling to soot or durcb vinyl chloride formation, byproducts, to carbon and/or.

Tar deposition on the fixed bed catalyst lead. The fixed bed catalyst must gradually hard becoming reaction conditions, like e.g. a rising Hydriertemperatur, exposed become, around its effectiveness obtained, until approx. 9 - 12 months these conditions of values reach, which make a renewal of the fixed bed catalyst required.

A regeneration of the consumed fixed bed catalyst is uneconomic. The precious metal recuperation is just as uneconomic, since the palladium contents are to low.

It was now surprisingly found that the described disadvantages of the prior art process by a method to the selective removal from acetylene with the vinyl chloride synthesis by cleavage of 1,2-Dichloräthan to ontstehenden and after the separation of the vinyl chloride remaining, predominant hydrogen chloride of contained gas mixture to be overcome be able, if one the gas mixture at a catalyst from a chemical inert orenarmen carrier material with a content of over 50 thread. < 0 SiO<sub>2</sub> of an average grain diameter above 0.3 mm, one

2 praying surface of bottom 5 m /g and a middle Porenvolumell below 0.01 ml/g, on which, related to the weight of the entire catalyst, more than 0.01 Gew.% of at least a metal from the group of the platinum metals applied is, with a wasserstoffhaltigen gas treated.

The method can become in wide ranges for temperature, pressure and flow rate performed.

A particularly economic operation regarding the Gesamt@erfahrens to the cleavage of 1,2-Dichloräthan plans, the gas mixture in a temperature range from 70 to 200 C to treat in particular between 120 and 1700 C with wasserstoffhaltigem gas whereby convenient pressures from normal pressure to 10 atue become, preferably from 6 to 7 atue applied.

The ratio from hydrogen to acetylene can between 1: 1 and 6: 1, vorz@gswise between 4: 1 and 5: are appropriate for 1.

The fixed bed catalyst required for the method knows a carrier material from at least 95 Gew.% SiO<sub>2</sub>, preferably gravel, with a praying surface of less than 3 m an average grain diameter from 1 to 10 mm, preferably 4 - 5 mm to be, on which the appropriately-used active metal is palladium in a possible concentration from 0,05 to 0.3 Gew.%, prefered 0.12 to 0.18 Gew.%, applied. ^ The catalyst required for the method can become prepared, by one e.g. that good washed and dried carrier material with a palladium chloride solution wetted, the chloride solution on the carrier material durch heating dries up and finally a reduction through-leads up from hydrogen makes. One appropriately fübrt one behind the other the Einzelstufen mentioned in a single apparatus (e.g. in a heatable rotary drum) with temperatures in the Bereich of 50 - 1500 Q, pressureless and/or. with light elevated pressure through.

The carrier material can thereby in the form of filling bodies (how; Raschig rings, Berlsätteln, spheres) or in irregular shape (e.g. Granulates) to the use come. Prefered one becomes as carrier material a feldspar-poor gravel, that in large amount in the commerce, e.g. as Filterkies, available is.

When chemical inert the carrier material bezeichnet because it with the peeling of the platinum group metal, e.g. with a Chlorwasserstoff402-Gemisch, not attacked becomes.

This is particularly favourable with an eventual workup of a consumed catalyst.

Surprisingly the V according to invention shows up > rfahren using surface and pore-poor SiO<sub>2</sub>-halti towards fixed bed catalyst substantial more effective as the method to the state of the art.

This behavior contradicts the prior general view that catalysts with carrier materials high praying surfaces and high pore volumes are maximum effective and selective.

The invention process can regard, - same hydrogenation temperatures presupposing the acetylene contents of crude hydrogen chloride as long time noch the bottom desired, lie close-conditional limit of 30 Vppm, while with the method in accordance with that states of the art disturbing acetylene contents is after short time over 70 Vppm.

Die gewünschte Hydrierung von Acetylen zu Äthylen wird von Anfang an wesentlich selektiver katalysiert als in dem Verfahren gemäss dem Stande der Technik. The undesirable attachment of

hydrogen chloride at acetylene can become by the method in accordance with invention significant reduced. The temperature range of the Versuchsreaktions can become during a very prolonged operational period between 1300 and 1400 C constant maintained.

A regeneration of the fixed bed catalyst brauchten in the invention process is to be accomplished economic worthwhile and technical light. The life of the fixed bed katalyseators in the method in accordance with invention is a mebrfaches prolonged around like that of the known catalyst.

The invention process becomes 2 more near explained on the basis the remark with of play. This becomes the example 1, which describes the method in accordance with the state of the art, against over-provided.

Example 1 (method in accordance with the state of the art): By a pilot reactor from stainless steel with the dimensions inner diameters: 12.5 cm length: 130.0 cms utilizable volumes: 15 1 becomes stündlich 10 N m<sup>3</sup> of a Robchlorwasserstoff gas of the approximate Zusammensetzung

99,5 Vol, % hydrogen chloride 150Nr -- 2500 Vppm acetylene

50 - 300 Vppm vinyl chloride

100 - 200 Vppm ethylen

50 - 100 Vppm methane from the method to the preparation of vinyl chloride through Cleavage of 1,2-Dichloräthan passed. In the reactor the pressure becomes constant maintained within the range of 6,5 - 6,7 atue. In the reactor entrance and in the reactor exit the current gas composition and the temperature of the gas become measured.

The reactor is filled with the fixed bed catalyst in accordance with the prior art process (5 1).

This has the characteristic data: Carrier material: Active alumina

Active metal: Palladium

Praying surface: 50 - 300 m

Pd - content: 0,1 - 0,2 Gew, %

Particle size 1 - 3 mm (strand presslings).

Additional ones become crude hydrogen chloride 0.8 Ni/h hydrogen into the reactor in-metered. An amount, which is about 3 time so high, like irn crude hydrogen chloride contained acetylene quantity.

The entire actual working time amounts to 140 days. The cleaned hydrogen chloride is re-used to the 1, 2-Dichloräthan-Herstellung.

Example 2 (Verfahren in accordance with invention): By a pilot reactor from stainless steel with the dimensions inner diameters: 12.5 cm length: 130.0 cms Nutzy2lumen: 15 1 werden stündlich 10 Nm eines Robchlorwasserstoffgases der Zusammensetzung: 99,5 Vol, % hydrogen chloride

1500 - 2500 Vppm acetylene

50 - 300 Vppm vinyl chloride

100 - 200 Vppm ethylen

50 - 100 Vppm Metban from the method for the production of vinyl chloride by cleavage of 1,2-Dichloräthan passed. In the reactor the pressure becomes constant maintained within the range of 6,5 - 6,7 atue.

In the reactor entrance the current gas composition and the temperature of the gas become measured.

The reactor is filled with the fixed bed catalyst in accordance with the method of the invention (5 1). Additional ones become crude hydrogen chloride 0.8 Ni/h hydrogen into the reactor in-metered. An amount, which is about 3 time so high, like the acetylene quantity contained in crude hydrogen chloride. The entire actual working time amounts to 140 days. Der gereinigte Chlorwasserstoff wird zur 1 , 2-Dichloräthan-Herstellung weiterverwendet.

A comparison of the two examples is all the confrontation of the results in the table 1 possible.

Table 1: (Part A)

EMI8.1

<September> Dimension <September> Example <September> 1 <September> Example  
 <September> 2  
 <tb> <September> Verfahren <SEP> after <September> invention <September> <September> Conditions <September> <September> gemäßes <September> <September> Feslaff  
 <September> Technology <September> drive  
 <tb> <SEP> Catalyst form <September> Strangpresslinge <September> Breakage  
 <tb> <September> " <September> - Particle size <September> mm <September> #  
 <September> 2; <September> 5-10 <September> 4-5  
 <tb> <September> " <September> - Surface <September> m/g <September> 220  
 <September> < 3  
 <tb> <September> Carrier material <September> Active alumina <September> Gravel  
 <tb> <September> Pd-content <September> on <September> Questioner <September> Gew,%  
 <September> 0.20 <September> 0.15  
 <tb> <September> In <September> Entrance <September> Vppm <September> 2,220  
 <September> 2,220  
 <tb> <September> In <September> Output <September> after <September> 1. <September> Day <September> " <SEP> < 3 <September> < 3  
 <tb> <September> " <September> " <September> 140. <September> "  
 <September> " <September> 73 <September> 9  
 <tb> <September> In <September> entrance <September> Vppm <September> 120  
 <September> 120  
 <tb> <September> In <September> Output <September> after <September> 1. <September> Day <September> " <September> 100 <September> 1.330  
 <tb> <September> " <September> " <September> 140. <September> "  
 <September> " <September> 810 <September> 1.540  
 <tb> <September> In <September> entrance <September> Vppm <September> < 3  
 <September> < 3  
 <tb> <September> In <September> Output <September> after <September> 1. <September> Day <September> " <September> 1,160 <September> 340  
 <tb> <September> " <September> " <September> 140. <September> "  
 <September> " <September> 210 <September> 230  
 <tb> Table 1 (part b) dimension example 1 example 2  
 EMI9.1

<September> In <September> Entrance <September> Vppm <September> < 3 <September> < 3  
 <tb> <September> In <September> Aingang.nach <September> 1. <September> Day  
 <September> " <September> not <September> certain <September> not <September> certain  
 <tb> <September> " <September> " <September> " <September> 140. <September> "  
 <September> " <September> 395 <September> 155  
 <tb> <September> In <September> Entrance <September> C <SEP> 130 <September> 130  
 <tb> <September> In <September> Output <September> after <September> 1. <September> Day <September> " <September> 130 <September> 130  
 <tb> <September> " <September> " <September> " <September> 140. <September> "  
 <September> " <September> 155 <September> 138  
 <tb> <September> Appearance <September> Stark <SEP> prepare <September> practical  
 <tb> <September> and. <September> bonded <September> unverändert  
 <tb> <September> C content <September> Gew,% <September> 25,0 <September> 0.2  
 <tb> <September> Annealing loss <September> (1 <September> h <September> 500 C)  
 <SEP> Gew,% <September> 44,0 <September> 1.5  
 <tb> <September> R@generierbarkeit <September> unwirtschaftl. <September> light  
 <September> possible  
 <tb> <September> Pd-recovery <September> unwirtschaftl. <September> "  
 <tb> Against the expectations, which were preserved opposite the method in accordance with that  
 states of the art, the method according to the invention shows the by far better experimental  
 results.

Thus acetylene contents in the example 2 can become also after 140 days noch the bottom erwunsobten plant-conditional limit of 30 Vppm maintained, during in the example 1 (state of the art) this acetylene limit value after 90 days over already walked becomes.

The erhnscste hydrogenation from acetylene to ethylen is in the example 2 from the outset substantial selective as in the example 1.

The undesirable attachment of hydrogen chloride at acetylene is in the example 1 substantial strong as in the example 2.

Experiment the temperature can in the example 2 during the 140 days duration of test constant between 130 - 1400 C maintained become, while it must become elevated in the example 1 gradually up to 155 C.

From the current registered measurement values estimated can become that the fixed bed catalyst of the invention process (example 2) has at least 3 time so long a life like the fixed bed catalyst in accordance with the method after that states of the art.

A comparison of the fixed bed catalysts is particularly impressive after 140 days attempt time: The fixed bed catalyst of the example 1 is sooted and bonded strong.

Experiments to the regeneration of the plague bed catalyst are fehlgeseblagen, and it is shown that a palladium recuperation cannot become from the consumed fixed bed catalyst because of the small palladium Gghaltes in economic manner conducted.

On the other hand the fixed bed catalyst of the example is 2 (methods in accordance with invention) unchanged and approximate just as effective as a fresh fixed bed catalyst after the same time.

A regeneration after longer operation proves than light possible. Also the palladium light and economic can be recovered worthwhile from the consumed catalyst.